Appendix F

Iterative Divergent/Convergent Approach to Conjugated Oligomers by a Doubling of Molecular Length at Each Iteration. A Rapid Route to Potential Molecular Wires
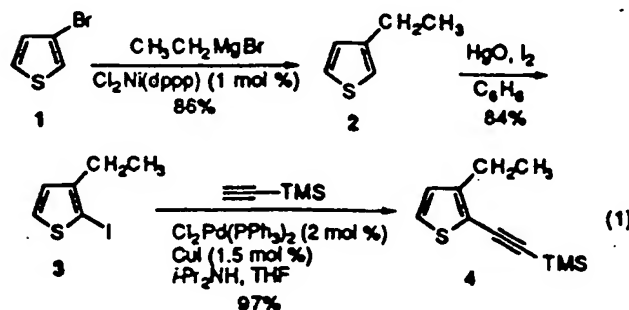
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The ultimate computational system would consist of logic devices that are ultradense, ultrafast, and molecular-sized.[1] Though bulk conjugated organic materials can indeed be semiconducting or even conducting,[2] electronic conduction based upon single or small packets of molecules has not been demonstrated and it is theoretically controversial.[1,3] Present nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100-Å gap regime.[4] In an attempt to span this 100-Å gap with molecules and to assess the feasibility of molecular wire conduction, we describe here a rapid synthetic approach to potential molecular wires based on an oligo(thiophene–ethynylene) derivative.[5,6] Additionally, these compounds possess properties that could make them useful for understanding bulk polymeric material properties.[7]

The synthesis of the key monomer 4, whose length will double at each stage, is outlined in eq 1.[8] The iterative

$$
\text{(1)}
$$

divergent/convergent synthetic approach is outlined in Scheme 1. The sequence involves partitioning 4 into two portions; iodinating the 5-position in one of the portions to form 5 and protodesilylating the alkynyl end of the second portion to form 6. Bringing the two portions back together in the presence of a Pd/Cu catalyst[8c–f] couples the aryl iodide to the terminal alkyne, thus generating the dimer 7. Iteration of this reaction sequence doubles the length of the dimer 7 to afford the tetramer 10, and so on to the octamer 13, and finally the 16-mer 16. The 16-mer, in its minimum-energy conformational form, has a molecular length of approximately 100 Å.[9]

The monomer through 16-mer, 4, 7, 10, 13, and 16, have been characterized spectroscopically. While the tetramer 10 and octamer 13 afforded molecular ions by direct exposure via electron impact mass spectrometry (MS), neither this method nor FAB or electrospray MS sufficed for obtaining a molecular ion of 16. However, matrix-assisted laser desorption MS did afford an M + 1 peak
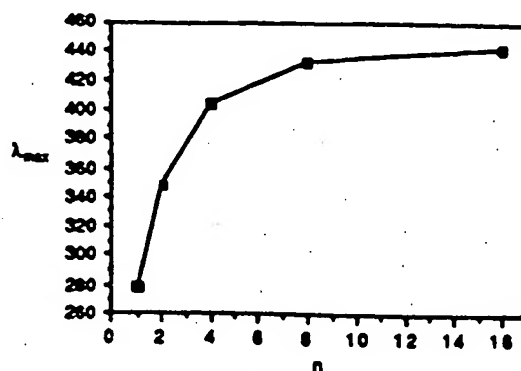

Figure 1. Optical absorbance maximum (λ_{max}) in CH_2Cl_2 versus the number of units in the oligomer (n) for 4, 7, 10, 13, and 16.
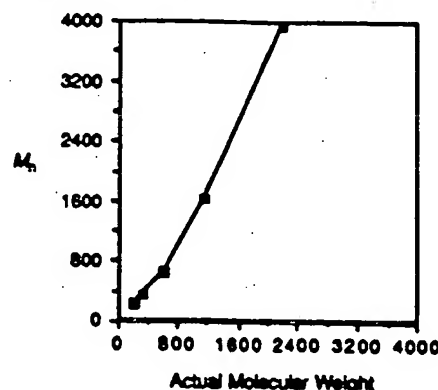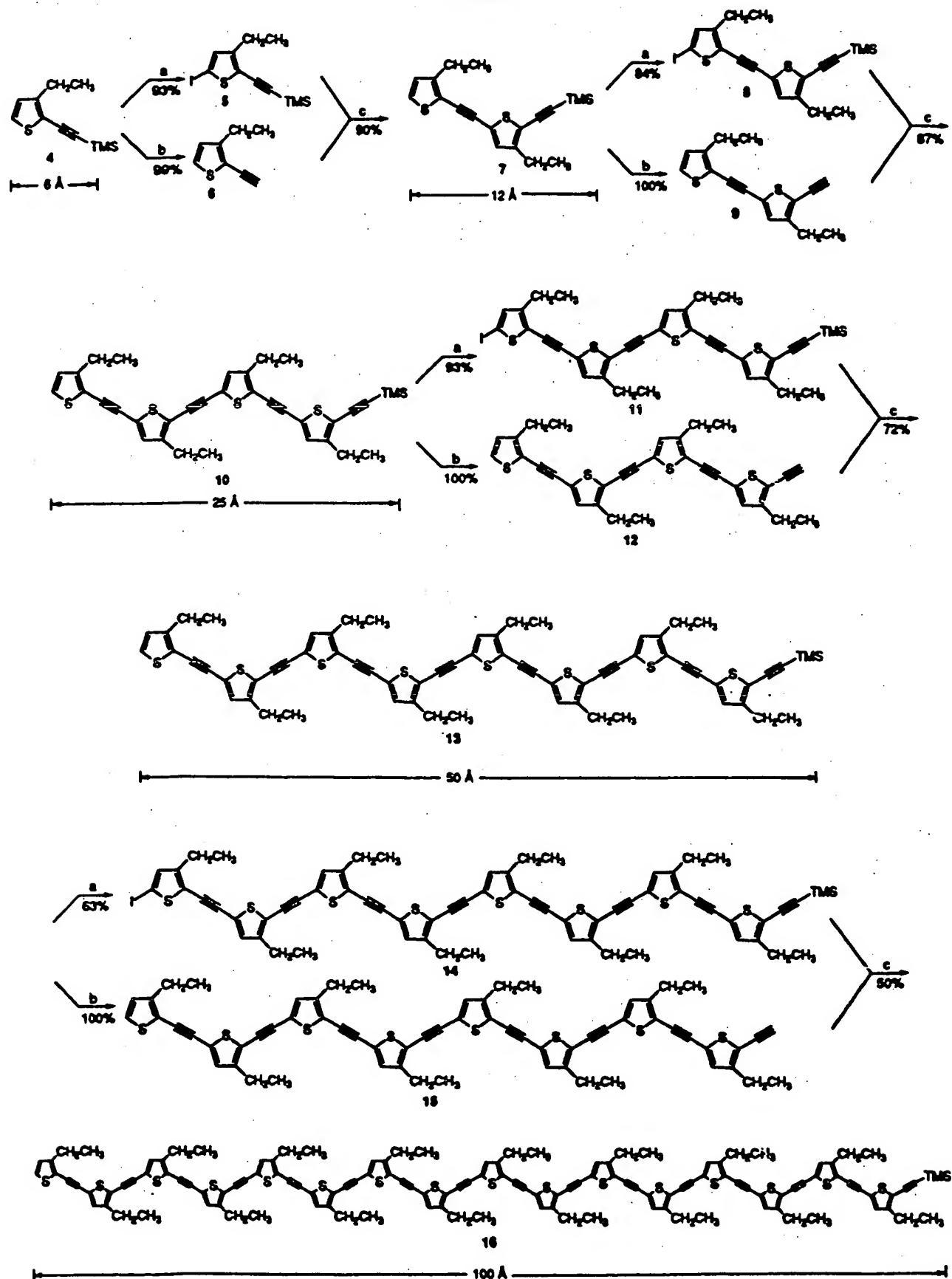

Figure 2. Values of M_n determined by SEC in THF (relative to polystyrene standards) versus the actual molecular weights of the monomer through 16-mer, 4, 7, 10, 13, and 16, respectively.

for 16 (sinapinic acid matrix, positive ion mode, M + 1. Calcd for $C_{131}H_{106}S_{16}Si$ + 1: 2222.32. Found: 2219.98 ± 1.20).

The optical spectra are interesting in that a near saturation of the systems appears to have occurred by the octamer stage so that doubling the conjugation length to the 16-mer caused little change in the absorbance maximum (Figure 1). The results of the size-exclusion chromatography (SEC) are also quite intriguing (Figure 2). SEC is not a direct measure of molecular weight but a measure of the hydrodynamic volume. Thus, by SEC using randomly coiled polystyrene standards, the number-average molecular weights (M_n) of rigid-rod polymers are usually greatly inflated relative to the actual molecular weights (MW). Accordingly, the SEC-recorded M_n values of the octamer (13; M_n = 1610, actual MW = 1146) and 16-mer (16; M_n = 3950, actual MW = 2218) were much greater than the actual MWs. Conversely, the monomer (4) through tetramer (10) had M_n values that were very close to the actual MWs (slope ~1.0 in Figure 2) because they are in the low–MW region, prior to significant polystyrene coiling. Therefore, Figure 2 could serve as a useful calibration chart for determining the MW of rigid-rod polymers. In all cases, the SEC-determined values of M_w/M_n = 1.02–1.05 were within the detectable range limits.

Scheme 1

Reagents: (a) LDA, Et₂O, -78° to 0°C then I₂, -78°. (b) K₂CO₃, MeOH, 23°C. (c) Cl₂Pd(PPh₃)₂ (2 mol %), CuI (1.5 mol %), THF, *i*-Pr₂NH, 23 °C.

Supplementary Material Available: Detailed synthetic procedures and characterization data for conversion of 1 to 16 (7 pages). Ordering information is given on any current masthead page.

References and Notes

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(9) The minimization was done using MMX with extended π-Hückel and multiconformational parameters (10° arylalkynyl bond rotational steps).